

Compact, orthogonal, and complete basis sets for solving the Schrodinger equation

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We present a new type of basis set which is local, compact, and orthogonal. The basis functions, called orthlets, are centered at the sites of a lattice and are specifically adapted to represent the system being studied. The adaptability includes the ability to have singular behavior within an orthlet, allowing a single orthlet to represent a function in the vicinity of a singularity.

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Most modern numerical solution techniques to the Schrodinger equation begin with the introduction of a basis set, thereby making an infinite Hilbert space finite. Because there are a number of incompatible qualities one would like in a basis set, a wide variety of basis sets are in use, each of which is better behaved according to some set of criteria. Among the desirable qualities are orthogonality, locality, compactness (i.e. compact support), the ability to represent space uniformly, the ability to represent singular regions with higher resolution, the ability to incorporate prior knowledge about singular regions, the ability to ignore empty regions, and the availability of specialized efficient algorithms (such as the fast fourier transforms (FFTs) or wavelet transforms) for doing integrals and solving differential equations.

For example, in electronic structure calculations for solids using density functional methods, plane waves are widely and successfully used [1]. These are orthogonal, have uniform resolution, and the FFT allows rapid switching between real and fourier space. Pseudopotentials are normally used to represent atomic cores. However, for more accurate treatment of the cores, for non-periodic systems (including molecules and surfaces), and for more accurate treatment of interatomic correlations, the plane wave basis is inconvenient.

In quantum chemistry, the standard choice for basis functions is the product of a radial function centered on an atom times a cartesian or spherical harmonic [2]. Because the radial functions which solve the Hartree Fock equations for atoms are known, remarkably small numbers of basis functions are needed—often only about twice as many basis functions as there are electrons. The nonorthogonality of the basis is easily dealt with in Hartree Fock. The major drawbacks relate to scaling to large systems and to high accuracy. The number of two-electron integrals needed to represent the inter-electron Coulomb interaction scales as N^4 , where N is the number of basis functions. Moreover, the orthogonalization required for most treatments of correlations beyond Hartree Fock destroys the approximate locality of the functions; consequently, computation time typically scales as N^6 or worse.

Wavelet bases are another potentially attractive alternative [3]. These nonorthogonal bases allow for widely

varying resolution to represent both cores and valence electrons. However, hundreds or thousands of wavelets on various length scales may be needed to represent a second row atomic core, compared to perhaps a dozen of the radial basis functions used in quantum chemistry,

In this letter, we propose a new type of basis set which is orthogonal, very localized and compact, which allows variable resolution, and which allows prior knowledge about singularities to be incorporated into the basis, while keeping the number of basis functions to a minimum. Our approach is most closely related to the finite element basis using orthogonal shape functions developed by White, Wilkins, and Teter (WWT) [4]. The major problem with the approach of WWT was the difficulty in obtaining adequate resolution for the cores. Our new approach overcomes that difficulty. Although these bases were developed with electronic structure calculations in mind, we expect them to be useful in a variety of other contexts as well.

Consider a set of localized *shape* functions $\phi_i(\vec{r})$, and a lattice $\{\vec{R}_j\}$. We can generate a set of functions for each lattice site by translation, $\phi_{ij} = \phi_i(\vec{r} - \vec{R}_j)$. Let the functions have the following properties: 1) the set of functions $\phi_i(\vec{r})$ is orthonormal; 2) each function is also orthogonal to the functions on all other lattice sites; and 3) the total set of functions on all lattice sites is *complete*. (Wannier functions also have these properties.) We define a projection operator for site j by

$$P_j = \sum_i |\phi_{ij}\rangle \langle \phi_{ij}|. \quad (1)$$

In coordinate notation this operator is

$$P_j(\vec{r}, \vec{r}') = \sum_i \phi_i(\vec{r} - \vec{R}_j) \phi_i(\vec{r}' - \vec{R}_j), \quad (2)$$

where the ϕ_i are assumed real. Completeness implies that $\sum_j P_j = 1$. Now consider the application of P_j on an arbitrary function $f(\vec{r})$: $f_j(\vec{r}) = P_j f(\vec{r})$. Then

$$f(\vec{r}) = \sum_j f_j(\vec{r}), \quad (3)$$

and

$$\langle f_j(\vec{r}) | f_{j'}(\vec{r}) \rangle = 0, \quad j \neq j'. \quad (4)$$

We will call functions such as $f_j(\vec{r})$, which are local, orthogonal, and specifically adapted to a function or to a set of functions, *orthlets*. The basis formed by the orthlets $f_j(\vec{r})$ is in a sense a perfect basis for representing $f(\vec{r})$: it is orthogonal, represents the function exactly, and has the minimum number of functions given the scale set by the lattice spacing. We describe below how to form an orthlet basis describing an arbitrary *set* of functions $f^\alpha(\vec{r})$ to a specified accuracy.

In order for the orthlets to be useful, the shape functions $\phi_i(\vec{r})$ should be smooth and local, and preferably compact. In two or more dimensions, shape functions can be written as products of one dimensional shape functions [4], so that we need only consider the 1D case. WWT developed a set of four shape functions with continuous derivatives up to third order, which were able to represent exactly polynomials up to third order [4]. These shape functions were compact, with a total width of two, where we assume a lattice spacing of unity henceforth. The compactness means that orthogonality must only be specifically arranged for nearest neighbor functions. Here we give six orthogonal shape functions which are smooth, i.e. all derivatives are continuous, which also are compact with width two, and which are able to represent polynomials exactly up to order five. We believe these shape functions are sufficiently complete for most uses, because we give alternative ways of generating the orthlets in the vicinity of singularities and also for changing lattice spacings. The smoothness allows additional functions to be added to increase completeness without adjusting the functions one already has.

All shape functions $S_n(x)$ are defined for $x \geq 0$; $S_n(x)$ is even (odd) if n is. We construct $S_0(x)$ to represent a constant function exactly. We first define a smooth “splicing function” $p(x)$ which divides a function to be fit to into pieces. We require that $p(x) = 0$ for $|x| \geq 1$, $p(x) = p(-x)$, and that

$$p(x) + p(x-1) = 1 \quad 0 \leq x \leq 1. \quad (5)$$

We choose the function

$$p(x) = \frac{1}{2} - \frac{1}{2} \tanh\left(\frac{3}{2} \frac{x-1/2}{[x(1-x)]^{1/2}}\right) \quad 0 < x < 1. \quad (6)$$

This bell-shaped function has essential singularities at $x = 0, \pm 1$, allowing it to have compact support yet be smooth.

The shape function is obtained by multiplying the function to fit to, in this case unity, by $p(x)$, and then adding a smooth oscillating function $o(x)$ to induce orthogonality. The fit will not be spoiled if

$$o(x) + o(x-1) = 0 \quad 0 \leq x \leq 1. \quad (7)$$

We choose

$$o(x) = \sum_{m=1}^M a_{0m} o_m(x) \quad (8)$$

where

$$o_m(x) = p(2x-1) \sin(2m\pi(x-1/2)). \quad (9)$$

For the first shape function, $S_0(x)$, it suffices to take $M = 1$, with $a_{01} = -0.507021142747521$:

$$S_0(x) = p(x) + a_{01} o_1(x) \quad 0 \leq x \leq 1. \quad (10)$$

Note that $S_0(x) + S_0(x-1) = 1$ for $0 \leq x \leq 1$, so that $S_0(x)$ is already normalized. We show $S_0(x)$ in Fig. 1(b).

The second shape function is obtained similarly, by requiring an exact fit to the function x . First, we attempt to fit the function x using only $S_0(x)$. We then make $S_1(x)$ out of the error or residual of this fit,

$$r_1(x) = x - S_0(x-1) \quad 0 \leq x \leq 1. \quad (11)$$

In this case, the extra orthogonalizing functions must be made out of cosine functions rather than sine functions, because the function itself is odd. For $0 \leq x \leq 1$

$$S_1(x) = N_1 \left(p(x) r_1(x) + \sum_{m=1}^2 a_{1m} e_m(x) \right), \quad (12)$$

with $S_1(-x) = -S_1(x)$,

$$e_m(x) = p(2x-1) \cos((2m-1)\pi(x-1/2)), \quad (13)$$

$a_{11} = 0.132403793351197$, $a_{12} = -0.048844623781880$, and $N_1 = 3.78750743638139$.

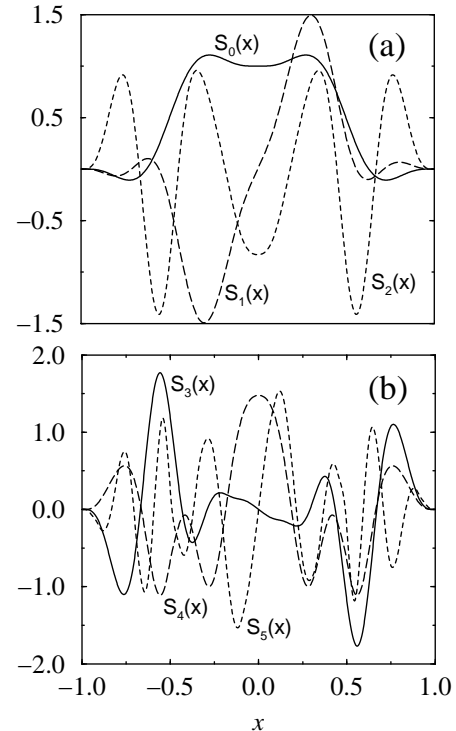


FIG. 1. (a) and (b) Shape functions $S_n(x)$.

To determine the coefficients a_{1m} , and later coefficients for higher order shape functions, two different linear combinations of the $e_m(x)$ or $o_m(x)$ were found which induced orthogonality to all the lower order shape functions centered at $x = 1$. These two different combinations were then combined in order to induce orthogonality of $S_n(x)$ and $S_n(x - 1)$. This last procedure required solving a quadratic equation, which might not have real roots. If there were no real roots, more orthogonalizing functions were included. A solution in this case required finding both positive and negative eigenvalues of a symmetric matrix, which also sometimes did not occur. There does not appear to be any guarantee of a real solution; in fact, we did not find a satisfactory $S_6(x)$ able to fit x^6 exactly.

The next shape function is given by

$$S_2(x) = N_2[p(x)(x^2 - c_{20}S_0(x) - d_{20}S_0(x - 1) - d_{21}S_1(x - 1)) + a_{21}o_1(x) + a_{22}o_2(x) + a_{23}o_3(x)], \quad (14)$$

$c_{20} = 0.0697096675548214$, $d_{20} = 1.0697096675548214$, $d_{21} = 0.528051768503122$, $a_{21} = 0.088401702549656$, $a_{22} = -0.126644764032427$, $a_{23} = -0.025357986069321$, and $N_2 = 11.9312518524753$. Expressions for S_3 to S_5 will be presented elsewhere [5].

In Fig. 2, we use these shape functions to generate an orthlet basis for a function with a slope discontinuity. For the lattice sites away from the singularity, the overlap integral of the function with each shape function was computed numerically. Resumming the shape functions on a site with these integrals as coefficients gives the orthlet. In the case of the orthlet at $x = 0$, where the slope discontinuity is, an expansion would converge too slowly. Instead, the orthlet was obtained by subtracting from $f(x)$ the orthlets on the adjacent sites.

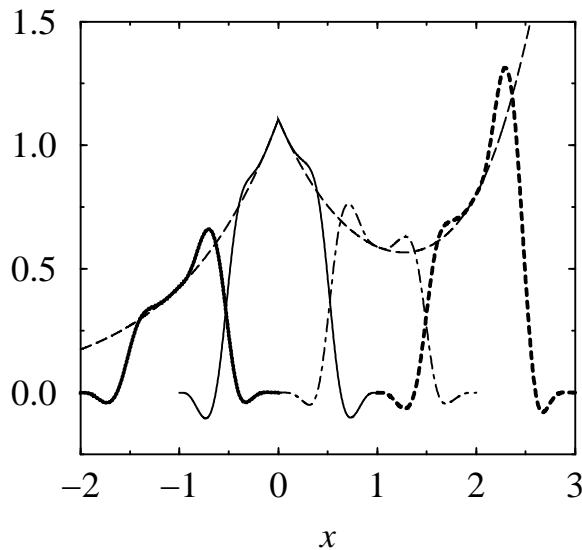


FIG. 2. Orthlets used to fit the function $f(x) = \exp(-|x|) + 1/((x - 3)^2 + 1/2)$. The sum of these four orthlets is equal to $f(x)$ within the region $-1 \leq x \leq 2$.

If the shape functions describe the function perfectly in the region away from the singularity, then the subtracted function will be identically zero for $|x| \geq 1$. If the fit is not perfect but very good, the function can be set to zero for $|x| \geq 1$. However, a small discontinuity and a small lack of orthogonality can result from this procedure. In this example, the discontinuities were less than 10^{-5} and were ignored, along with a small nonorthogonality. In order to ensure perfect continuity and orthogonality in this example, we could multiply the subtracted function by a smooth windowing function which is unity for most of the interval $-1 \leq x \leq 1$, and is zero for $|x| \geq 1$. Then the resulting function can be explicitly orthogonalized in a Gram-Schmidt (GS) procedure to the neighboring shape functions. Because of the orthogonalization, the resulting function would extend from $-2 \leq x \leq 2$.

Another procedure for dealing with singularities is to add a set of localized functions near the singularity, which are chosen for their ability to represent the singularity. Then an explicit GS orthogonalization procedure mixes these functions with the shape functions that overlap them. This GS procedure does not destroy overall locality: all shape functions not directly overlapping the functions added would still automatically be orthogonal to the new set of functions. Orthlets are then formed as linear combinations of the shape functions and the added singularity functions. In three dimensions, we form shape functions as cartesian products of the 1D shape functions, $S_{\vec{n}}(\vec{r}) = S_{n_x}(x)S_{n_y}(y)S_{n_z}(z)$. In preliminary calculations to represent the hydrogen atom ground state, we have found that adding a set of narrow gaussians, multiplied by a windowing function similar to $p(x)$, is very convenient and effective for representing the cusp singularity at the nucleus. Part of the convenience is that 3D gaussians are products of 1D gaussians, like the 3D shape functions. These results will be presented elsewhere.

There are several ways to change the basic lattice spacing in different regions of space. One simple approach is to let the finer and coarser grids overlap, so that completeness is ensured, and then apply a GS procedure to the overlap region, automatically generating local functions which connect the two regions. However, the ability to generate orthlets with singularities means that changing the lattice spacing is usually not necessary.

Now, suppose one wishes to generate orthlets to represent a set of functions $\{f^\alpha(\vec{r})\}$. For example, one might want to build an orthlet basis which is able to represent a standard radial basis set from quantum chemistry, since these basis sets are known to represent Hartree Fock orbitals well. Note that the f_α need not be orthogonal, but the orthlet basis generated from them is. The orthlet basis will automatically have additional degrees of freedom allowing improved treatment of correlations. For simplicity, we will let $S_{\vec{n}}(\vec{r})$ represent both shape functions and any extra singularity basis functions. To adapt the basis to represent the f_α , we apply the procedure in

the density matrix renormalization group for targeting more than one state [6]. For each lattice site j , we find the coefficients

$$c_{\alpha\vec{n}} = \langle S_{\vec{n}}^j(\vec{r}) | f_{\alpha}(\vec{r}) \rangle. \quad (15)$$

We now form the positive semidefinite density matrix

$$\rho_{\vec{n}'\vec{n}}^j = \sum_{\alpha} c_{\alpha\vec{n}'} c_{\alpha\vec{n}}. \quad (16)$$

Note that positive weighting factors a_{α} can also be included in the sum if some of the functions are considered more important than others. The eigenvectors of ρ^j , $v_{\vec{n}}^{\beta}$, define orthlet functions $v^{\beta}(\vec{r}) = \sum_{\vec{n}} v_{\vec{n}}^{\beta} S_{\vec{n}}^j(\vec{r})$ which optimally represent the functions $\{f_{\alpha}(\vec{r})\}$ in the basis for site j . Each density matrix eigenvalue w_{β} gives the weight associated with that orthlet in representing the f_{α} . By choosing a cut off weight, and retaining all orthlets with weight greater than the cut off, one obtains a systematically improvable basis for the f_{α} . In particular, one can show that

$$w_{\beta} = \sum_{\alpha} (\langle v^{\beta} | f_{\alpha} \rangle)^2. \quad (17)$$

Thus, if a density matrix eigenvalue w_{β} is very small, then none of the f_{α} have significant overlap with the corresponding function v^{β} , and v^{β} need not be included in the basis. The basis set becomes exact if the number of orthlets kept per site is equal to the number of functions f_{α} . If only one function is in the set f_{α} , then there is only one nonzero eigenvalue and the orthlet is simply the normalized projected function $P_i f_{\alpha}$.

As an example of this procedure, we generate a general set of orthlets to use as a basis set for the tails of wavefunctions. The ordinary shape functions are too localized to represent an exponentially decaying tail efficiently. The orthlets we generate here extend quite far in one direction, and so are very useful to use as replacements for the shape functions for the edge sites of the lattice, allowing fewer sites to be used. The functions are constructed by using as f_{α} a set of 13 gaussians with widths ranging from 1 to 4, each centered at the origin, constructing and diagonalizing the density matrix. The basis for an orthlet includes more than one site here: we include all 78 shape functions on sites 3 to 15. The resulting orthlets are able to represent any linear combination of the 13 gaussians with good accuracy. The three most important functions, along with the density matrix eigenvalues w_{β} , are shown in Fig. 3. One can see the the density matrix eigenvalues decay very rapidly, so that only a few of these orthlets are needed.

In electronic structure calculations, one would use a lattice spacing appropriate for the valence electrons, say 0.3-1.0 angstroms. Cores would be treated using orthlets derived from localized cusp functions, which would be tied to each nucleus.

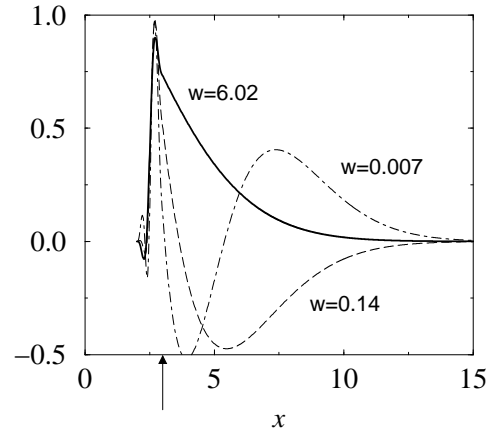


FIG. 3. Orthlets which can be used to represent tails of wavefunctions. The orthlets are adapted to a set of 13 gaussians centered at 0 with a variety of widths. The density matrix eigenvalue w of each orthlet is given. The arrow indicates the location of the first site (3) included in the basis for the orthlets. The functions are orthogonal to all shape functions to the left of that site.

Lattice sites near cores would have a dozen or more orthlets; in other areas, we expect only a few might be needed, making perhaps 100-300 basis functions per atom. Although this is an order of magnitude more than with the radial functions used in quantum chemistry, it is perhaps an order of magnitude less than a wavelet basis, and the orthlets would be orthogonal and compact. The orthlets appear to be very convenient for the development of $o(N)$ algorithms for density functional calculations; for example, sparse matrix methods coupled with the multigrid algorithm might be used to solve the Poisson equation. Orthlets also appear well adapted to multipole representations of the electron-electron interaction, which can also be used in $o(N)$ algorithms.

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